

# PATENT ABSTRACTS OF JAPAN

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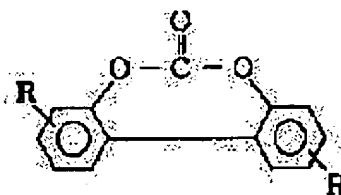
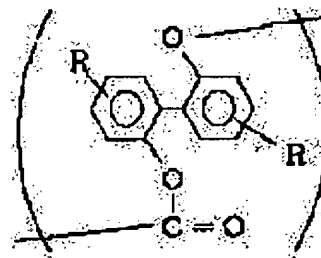
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## (54) AROMATIC POLYCARBONATE AND PRODUCTION THEREOF

### (57)Abstract:

**PURPOSE:** To obtain an aromatic polycarbonate which is usable as a tough polymer under ordinary conditions and degrades at an elevated temp. to enable the recovery of the monomer therefrom in a pure state, by constituting the polycarbonate of a specific repeating unit and specifying the intrinsic viscosity.

**CONSTITUTION:** The aromatic polycarbonate is substantially made up of repeating units represented by formula I (wherein R is H, a halogen, or a 1-5C alkyl) and has an intrinsic viscosity as measured at 35°C in a 60:40 (by weight) mixture of phenol and tetrachloroethane of 0.2 or higher. It is obtained by polymerizing a cyclic carbonate represented by formula II (wherein R is as defined above) by ring opening polymerization using 0.001-5mol% initiator in the presence or absence of a solvent.



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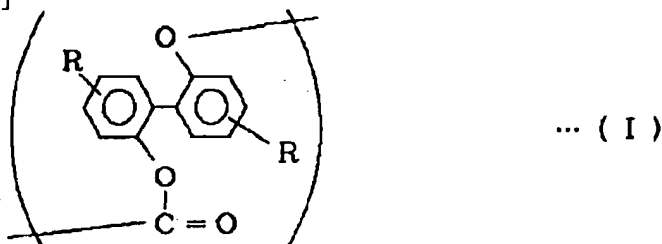
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## CLAIMS

[Claim(s)]

[Claim 1] The aromatic series polycarbonate characterized by being the aromatic series polycarbonate which becomes substantial from the repeat unit expressed with the following type (I), and the intrinsic viscosity measured at 35 degrees C among the mixed solvent of a phenol/tetrachloroethane (weight ratios 60/40) being 0.2 or more.

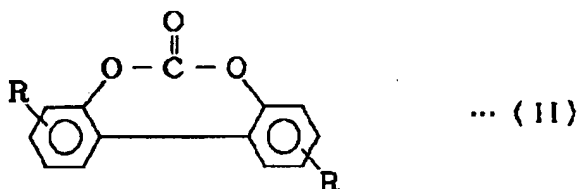
[Formula 1]



[但し、Rは水素、ハロゲンまたは炭素数1～5の低級アルキルを示す]

[Claim 2] The manufacturing method of the aromatic series polycarbonate which consists of a repeat unit expressed with the above-mentioned formula (I) characterized by carrying out ring opening polymerization of the annular carbonate compound expressed with the following type (II) under existence of a solvent or nonexistence using 0.001 - five-mol % of an initiator to this annular carbonate compound.

[Formula 2]



[但し、Rは水素、ハロゲンまたは炭素数1～5の低級アルキルを示す]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a new aromatic series polycarbonate and its manufacturing method. Near a room temperature, it is related with the approach of manufacturing a new aromatic series polycarbonate and this aromatic series polycarbonate with the recycle nature which can decompose if it can be used as a polymer of high intensity and made an elevated temperature, and can collect pure raw materials, in more detail.

[0002]

[Description of the Prior Art] Various examination about the recycling of a polymer is performed from a viewpoint of current and earth environmental protection. however, when it collects and recycles as a polymer, it is difficult to remove various mixture -- etc. -- a recycle polymer tends to become the thing of low quality from a reason compared with the polymer compounded at first Moreover, in collecting as a raw material, it is necessary to perform various chemical preparation the middle, and becomes cost quantity from the case where a raw material is manufactured newly, in many cases.

[0003]

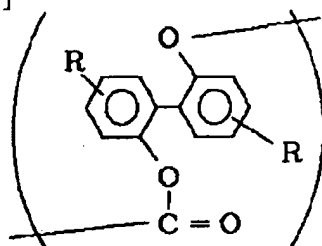
[Problem(s) to be Solved by the Invention] The 1st purpose of this invention is under anticipated-use conditions to offer the polymer which can use as a tough polymer and can be collected as a raw material by simple actuation. Moreover, the 2nd purpose of this invention is to offer the approach of manufacturing this polymer industrially.

[0004]

[Means for Solving the Problem] The purpose of this invention like \*\*\*\* is the following type (I).

[0005]

[Formula 3]



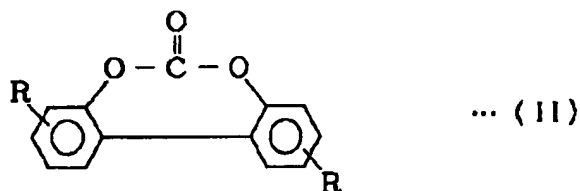
... ( I )

[但し、Rは水素、ハロゲンまたは炭素数1～5の低級アルキルを示す]

[0006] The aromatic series polycarbonate characterized by being the aromatic series polycarbonate which comes out and consists of repeat units expressed substantially, and the intrinsic viscosity measured at 35 degrees C among the mixed solvent of a phenol/tetrachloroethane (weight ratios 60/40) being 0.2 or more, and the following type (II)

[0007]

[Formula 4]



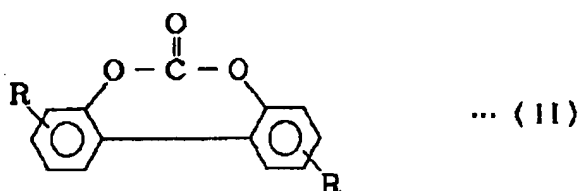
[但し、Rは水素、ハロゲンまたは炭素数1～5の低級アルキルを示す]

[0008] Therefore, it is attained by the manufacturing method of the aromatic series polycarbonate characterized by coming out and carrying out ring opening polymerization of the annular carbonate compound expressed under existence of a solvent or nonexistence using 0.001-5-mol % of an initiator to this annular carbonate compound.

[0009] Hereafter, this invention is explained in full detail. The manufacturing method of the aromatic-series polycarbonate which consists of a repeat unit shown by the above-mentioned formula (I) concerning this invention can illustrate the approach of manufacturing, while, removing the hydrogen chloride which generates 2 and 2'-dihydroxydiphenyl and a phosgene during a reaction by making alkali live together in the system of reaction etc. for example, the approach of manufacturing by carrying out ring opening polymerization of the annular carbonate compound shown by the (ii) following formula (II), etc., although especially limitation is not carried out.

[0010]

[Formula 5]



[但し、Rは水素、ハロゲンまたは炭素数1～5の低級アルキルを示す]

[0011] Moreover, about the polymerization degree of a polymer, if polymerization degree is too small, in order not to acquire sufficient physical properties but for polymer decomposition temperature to also fall, it is necessary to have the polymerization degree which makes it preferably the intrinsic viscosity measured at 35 degrees C among the mixed solvent of a phenol/tetrachloroethane (weight ratios 60/40), and becomes 0.2 or more. It is more desirable that this intrinsic viscosity is 0.3 or more in this invention, and it is desirable that it is especially 0.4 or more.

[0012] In addition, although it is desirable that it is a hydrogen atom as for R in the above-mentioned (I) formula and the (II) type, it may be the low-grade alkyl of the carbon numbers 1-5, such as halogens, such as chlorine, a bromine, and a fluorine, and methyl, ethyl, propyl, isopropyl. Moreover, it does not need to be altogether the same, and the substituent (R) of a nucleus makes R in most repeat units a hydrogen atom, and is good also considering R in some repeat units as a halogen or low-grade alkyl.

[0013] Moreover, other little polymer repeat units may be copolymerized in the range to which the property of this polymer is not essentially changed, or various kinds of additives may be added.

[0014] Next, the advantageous manufacturing method of the aromatic series polycarbonate of this invention is explained in full detail. By this invention approach, the aromatic series polycarbonate which has the repeat unit expressed with the above-mentioned formula (I) is manufactured by carrying out ring opening polymerization of the annular carbonate compound shown by the above-mentioned formula (II). Although there is especially no limit in the temperature of the ring-opening-polymerization reaction at the time of manufacturing this polymer, if it becomes an elevated temperature not much, since the polymer with the repeat unit shown by the above-mentioned formula (I) tends to return to the annular

carbonate compound of the following formula (II), it will become difficult to obtain a high-polymer polymer. Then, as temperature at the time of manufacturing a polymer, it is desirable that it is 160 degrees C or less, it is more desirable that it is 100 degrees C or less, and it is most desirable that it is 40 degrees C or less. Moreover, although either can perform a reaction under existence of a solvent or nonexistence, to manufacture under solvent existence is more desirable.

[0015] As a solvent, although there is especially no limit, it can illustrate chloroform, tetrachloroethane, chlorobenzene, N-methyl pyrrolidone, N, and N-dimethylacetamide, dimethyl sulfoxide, a sulfolane, etc., and can illustrate dimethyl sulfoxide, a sulfolane, etc. as a desirable solvent especially.

[0016] In the polymerization method of this invention, the most important point is the amount of initiators which exists in the system of reaction. Since the point used as a reaction end will increase or an annular carbonate compound will decompose if there are too many amounts of initiators which exist in the system of reaction of a polymerization reaction, polymerization degree will not go up. Moreover, when there are too few amounts of initiators, there are few points which start ring opening reaction, the case where all the active spots deactivate with an impurity etc. increases, and it is hard coming to go up polymerization degree. Then, as an amount of initiators which exists in the system of reaction, it is required to be 0.001-5-mol % to an annular carbonate compound, it is desirable that it is [ 0.001-4 mol ] %, and it is [ it is more desirable that it is / 0.01-3 mol / %, and ] most desirable that it is [ 0.1-2 mol ] %.

[0017] As an initiator, a general anionic polymerization catalyst, water, etc. can be illustrated, for example, and sodium methoxide, a sodium ethoxide, potassium-t-butoxide, a sodium phenoxide, n-butyl lithium, etc. can be illustrated as a desirable anionic polymerization catalyst.

[0018] This time amount changes with reaction time, reaction scales, etc. that reaction time should just be time amount to which the above-mentioned polymerization reaction is sufficient for fully going on. It is about 2 - 100 hours more preferably for 1 to 200 hours.

[0019] The polymer which has the repeat unit shown by the following formula (I) can obtain tough mold goods by the general melting fabricating method and the general film cast method. Moreover, since a by-product does not generate in manufacturing a polymer with the repeat unit shown by the above-mentioned formula (I) from the annular carbonate compound of the above-mentioned formula (II), when it manufactures under the nonexistence of a solvent, it can be used also as reaction molding resin.

[0020] Moreover, it will decompose, if it is made the elevated temperature beyond anticipated-use temperature at a surprising thing, and the aromatic series polycarbonate of this invention has the property which returns to the annular carbonate compound expressed with the above-mentioned formula (II), and can collect these annular carbonate compounds as a raw material. It is desirable that it is 200 degrees C or more as decomposition temperature, it is more desirable that it is 230 degrees C or more, and it is most desirable that it is 260 degrees C or more. By furthermore making a system reduced pressure, the annular carbonate compounds of the above-mentioned formula (II) can be collected more promptly.

[0021] The polymer of this invention can be identified in the analysis by measurement of the melting point and glass transition temperature, IR, NMR, etc.

[0022] In addition, the annular carbonate compound of the above-mentioned formula (II) used as a raw material by the approach of this invention It can manufacture easily by the approach this invention persons make the 2 and 2'-dihydroxydiphenyl previously proposed in Japanese Patent Application No. No. 124755 [ four to ], and diphenyl carbonate react to the bottom of existence of a catalyst by equimolar substantially. According to this approach, the target annular carbonate compound can be manufactured, without using a poisonous phosgene.

[0023]

[Effect of the Invention] As mentioned above, the aromatic series polycarbonate obtained by this invention can be used as a tough polymer near a room temperature. And by performing simple actuation of carrying out heating at high temperature, the annular carbonate which is a polymer raw material can be collected in a pure form, and the polymer of this invention is a polymer in which efficient polymer recycling is possible.

[0024] Moreover, according to the manufacture approach of this invention, it becomes possible to manufacture a desired aromatic series polycarbonate easily, without using a special catalyst and equipment.

[0025]

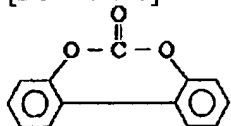
[Example] An example is given below and this invention is explained in full detail. That it is only with the "section" among an example means the "weight section."

[0026] Polymer intrinsic viscosity ( $\eta_{inh}$ ) is the value measured at the temperature of 35 degrees C using the phenol / tetrachloroethane mixed solvent (weight ratios 60/40). Moreover, DSC is used for the polymer melting point ( $T_m$ ) and glass transition temperature ( $T_g$ ), and they are the programming rate of 10 degrees C / min. It is the measured value.

[0027]

[Example 1] The annular carbonate compound 3 section expressed with the following type, [0028]

[Formula 6]



[0029] The dimethyl sulfoxide (DMSO) 30 section and (the water content of 105 ppm) were quickly put into the reaction container (it dries at 100 degrees C for 10 hours) which offered stirring equipment, the system of reaction and the open air were intercepted, and it stirred at the room temperature for 40 hours. Then, the reactant was supplied to the methanol, and the polymer which deposited in the system was washed and it dried. It was  $\eta_{inh}=0.8$  when the intrinsic viscosity of the obtained polymer was measured. The melting point of this polymer was 258.5 degrees C, and glass transition temperature was 132 degrees C.

[0030]

[Examples 2-8]  $\eta_{inh}$  of a polymer which changed and manufactured the water content of the solvent in an example 1 and a solvent, reaction time, and reaction temperature is shown in Table 1 as examples 2-8. In addition, in all reactions, the reaction container was dried at 100 degrees C for 10 hours or more. Moreover, all catalyst additions were made into one-mol % in the examples 7-8 which added the catalyst.

[0031]

[Table 1]

	溶媒	含水率 (ppm)	反応時間 (hr)	反応温度 (℃)	触媒	$\eta_{inh}$
実施例2	DMSO	183	18	0	無	0.62
” 3	”	75	20	室温	”	0.36
” 4	”	121	80	0	”	0.85
” 5	”	42	10	50	”	0.22
” 6	”	93	20	室温	”	0.41
” 7	”	115	12	”	ナトリウムトキシ	0.24
” 8	クロロホルム	105	8	”	水素化ナトリウム	0.21

[0032]

[Example 9] The sodium-methoxide 0.01 section was put into the reaction container (it dries at 100 degrees C for 10 hours) which offered stirring equipment as a catalyst with the annular carbonate

compound 3 same section as an example 1, the system of reaction was intercepted with the open air, and it stirred at 150 degrees C for 5 hours. Then, it was etainh=0.35, when the polymer was taken out of the reaction container and polymer intrinsic viscosity was measured.

[0033]

[Examples 10-12] etainh of a polymer which changed and manufactured the reaction temperature of an example 9, reaction time, and a catalyst is shown in Table 2 as examples 10-12. In addition, all the catalyst additions in these examples are one-mol %.

[0034]

[Table 2]

	反応温度 (℃)	反応時間 (時間)	触媒	$\eta_{inh}$
実施例10	110	2	水素化ナトリウム	0.45
" 11	150	3	水素化リチウム	0.38
" 12	200	5	炭酸カリウム	0.27

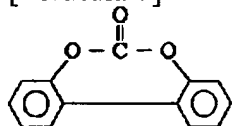
[0035]

[Example 13] The polymer 1 section manufactured in the example 1 was put into the glass tube with a die length of 15cm, from the pars basilaris ossis occipitalis, only die length of 1cm was given to the 270-degree C salt bath, and heated the glass tube, it was made reduced pressure with the vacuum pump, and when the interior of a glass tube was maintained at 2mmHg(s) and held for 20 minutes, the white crystal adhered to the glass tube upper part. Then, weight was the 0.9 sections when the crystals which returned the system of reaction to ordinary pressure, and adhered to the glass tube upper part were collected.

When IR of this thing, NMR, and the melting point were measured and analyzed, it was checked that it is the annular carbonate compound shown by the following formula.

[0036]

[Formula 7]



[Translation done.]